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(54) MANUFACTURE OF MALEIC ANHYDRIDE

- (71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German joint stock company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby
 5 declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
 10 This invention relates to a new continuous process for the manufacture of maleic anhydride on an industrial scale.
 It is generally known to manufacture maleic anhydride by oxidizing straight-
 15 chained unsaturated C₄ hydrocarbons such as butadiene, but-1-ene or but-2-ene or mixtures thereof with air in a tubular reactor in the presence of catalysts containing titanium dioxide, vanadium pentoxide and phosphorus pentoxide. Large-scale manufacture
 20 with its requirements of cheap raw material, good yields, smooth operation and constant quality of maleic anhydride is influenced by numerous factors which are partly inter-dependent and partly independent of each
 25 other.
 Due to the many parameters and the frequently unknown interrelationship between them, the optimum conditions for such a
 30 process can not be determined by systematic deduction. The present invention seeks to improve the process for the manufacture of maleic anhydride as outlined above such that it produces consistently high yields of
 35 product of consistent quality by readily controllable, trouble-free, large-scale procedures employing the cheapest starting materials.
 We have now found an improved process for the continuous manufacture of maleic
 40 anhydride by oxidizing a mixture of C₄ hydrocarbons with air in a tubular reactor in the presence of a catalyst containing titanium dioxide, vanadium pentoxide and phosphorus pentoxide, in which process the
 45 maleic anhydride formed is washed out of the reaction gases, the thus formed maleic acid is concentrated and then converted into maleic anhydride and water, and the maleic anhydride thus obtained is purified by continuous distillation, the improved process
 50 being characterized in that
 (a) a mixture of C₄ hydrocarbons is used which contains at least 50% by weight
 55 of unbranched olefinically unsaturated C₄ hydrocarbons, this mixture is added to air heated to from 100° to 200°C, whereupon a volatile inorganic or organic phosphorus compound is added,
 (b) this gas mixture is fed to a tubular
 60 reactor in which the tubes are packed with a catalyst containing from 45 to 95% of TiO₂, from 0.2 to 20% of V₂O₅ and from 3 to 53% of P₂O₅, by weight,
 (c) a temperature of from 420° to 600°C
 65 is maintained within the tubes, heat exchange being effected by a salt bath maintained at from 360° to 440°C, which salt bath is circulated through the reactor, evenly on all sides thereof, being
 70 fed to the reactor at one end through an annular channel and removed therefrom at the other end through a second annular channel,
 (d) the effluent reaction gases are cooled to
 75 from 160° to 180°C and fed to a washing powder, in which the maleic anhydride is washed out by a circulated, cooled, aqueous maleic acid solution, the resultant 30 to 50% by weight
 80 maleic acid solution is concentrated in one or more film evaporators arranged in cascade fashion to a concentration of more than 90% by weight and the concentrate is dissociated in a further film
 85 evaporator to form maleic anhydride and steam, the removal of the water of reaction being carried out without inert entraining agents by direct entrainment by maleic anhydride vapors, and the
 90 cooled maleic anhydride obtained by fractional condensation is continuously distilled in a distilling system.
 The aforementioned mixtures of C₄ hydrocarbons may, for example, be those produced

as a direct result of petroleum cracking and containing, by weight, at least 30%, for example from 30 to 60%, of butadiene, from 10 to 20% of but-1-ene, from 10 to 20% of but-2-ene, from 5 to 30% of isobutene and from 2 to 10% of n- and iso-butan-5

A considerable advance is achieved by using such C_4 cuts from which the valuable constituent butadiene and possibly also isobutene have been wholly or partly removed. Examples of such mixtures are those containing from 0 to 30% of butadiene, from 20 to 100% of n-butenes, from 0 to 40% of isobutene and from 10 to 50% of butanes, 15 by weight, the sum of butadiene and n-butenes being at least 50% by weight.

Suitable volatile organic or inorganic phosphorus compounds are all metal-free compounds which are sufficiently volatile at 200°C to allow from 2 to 50 mg thereof to be evaporated in 1 m³ of air (STP). This applies to virtually all phosphorus compounds, which, in addition, all behave in an equivalent fashion, since without exception they are converted to phosphorus pentoxide or phosphoric acid under the conditions of the reaction. For practical reasons, however, lower trialkyl phosphates are preferred, such as those having alkyl radicals of from 1 to 4 carbon atoms, because these are particularly easy to meter, are readily available and are non-corrosive. 20

In large-scale synthesis the crude C_4 mixture is suitably injected in an amount of from 25 to 40 g/m³, preferably 33 g/m³ (STP), into air heated to from 100° to 200°C. After the addition of suitably from 10 to 25 mg/m³ (STP) of a volatile phosphorus compound, preferably triisobutyl phosphate, the gas mixture is fed to the tubular reactor. The reactor is packed with a catalyst, which preferably consists of from 70 to 92% of TiO_2 , from 3 to 10% of V_2O_5 , and from 5 to 20% of P_2O_5 , by weight, and conveniently has the form of cylinders of from 4 to 8 mm in diameter and from 5 to 20 mm in length or in the form of spheres of from 4 to 8 mm diameter. 25

A suitable tubular reactor for the present process is, for example, one having from 5,000 to 10,000 tubes each having a diameter of from 25 to 40 mm. At each end of the reactor there is provided an annular channel—one for the introduction of the salt bath acting as coolant and the other for its removal. The annular channel communicates with the interior of the reactor through orifices. The coolant is a salt bath which is maintained at from 360° to 440°C in the reactor. When the temperature of the melt is within the limits stated, the maximum temperature in the catalyst zone—which occurs in the first half thereof (hot spot)—is maintained at from 420° to 600°C, and particularly at from 450° to 550°C. 30

The effluent gases from the tubular reactor are cooled in a heat exchanger, suitably either by the air which is to be heated and used in the process or by water, in which case steam is produced, such that the temperature of the gases after cooling lies between 160° and 180°C. The cooled gases are then fed to a washing tower, in which the maleic anhydride is washed out of the reaction gases by a circulated, cooled, aqueous maleic acid solution. During this operation the gases are normally cooled to about from 30° to 60°C. 70

The maleic acid solution which is continuously withdrawn from the washing tower has a concentration of 30 to 50% by weight of maleic acid. This is replenished at the same rate, likewise continuously, by fresh water or by dilute aqueous maleic acid solution obtained from the distillate produced at the anhydridizing stage. 75

The from 30 to 50% by weight maleic acid solution is concentrated to a concentration of more than 90% by weight in one or more falling film evaporators arranged in cascade fashion, suitably at a pressure of from 400 to 760 mm of Hg and a temperature ranging from 115° to 160°C, the residence time being less than 5 minutes. The concentrate is then immediately fed to another film evaporator, in which the residual water is evaporated, suitably at a pressure of from 50 to 700 mm of Hg and at a temperature of from 130° to 200°C, the residence time being less than 5 minutes, and in which the maleic acid is dissociated to maleic anhydride and steam. In the following fractional condensation crude maleic anhydride is obtained in a first condenser and this passes on for distillation, and in a second condenser there is produced an anhydride containing more than 2% by weight of water, and this is returned to the film evaporator in which dissociation was carried out. That proportion of the maleic anhydride which does not liquify due to its partial pressure is suitably washed out of the vapors with water. The resulting dilute maleic acid solution containing from about 2 to 5% by weight of maleic acid is passed, for concentration, to the washing tower used for washing the reaction gases. 80

Distillation of the crude maleic anhydride is conveniently carried out in a column at a temperature of from 100° to 180°C and a pressure of from 50 to 300 mm of Hg. The base of the column is connected to a circulation evaporator. The pure vaporous maleic anhydride is withdrawn from the middle portion of the column, and the low-boiling portions are driven off at the top. The non-volatile or difficultly volatile compounds are continuously centrifuged out of the base. 85

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The process of the invention makes it possible to use C_4 hydrocarbon mixtures which occur as necessary fractions in industrial operations and which have hitherto mainly been useful as fuels. Another important advantage is that only a few by-products are obtained during working up, but in the previously known processes fairly large quantities of by-products had to be tolerated, these being caused by the longer residence times during anhydridization using entraining agents.

The invention is further illustrated by the following Examples in which percentages are by weight.

EXAMPLE 1

20,000 m^3/h of air (STP), which has a temperature of about $100^\circ C$ due to the heat of compression, are passed, after the injection of 660 kg of crude C_4 mixture containing approximately 40% of butadiene, 25% of n-butenes, 25% of isobutene and 10% of butanes, to the top of a tubular reactor together with 500 g/h of isobutyl phosphate. The reactor contains 5,500 tubes having a diameter of 25 mm and a length of 3 m. The tubes are surrounded by a bath comprising molten saltpetre. At the bottom and top of the reactor there are provided annular channels for the introduction and removal respectively of the molten salt. The melt flows countercurrently to the gas stream, leaving the reactor at its top and being recycled to the bottom thereof after cooling.

The temperature of the melt is maintained at $420^\circ C$.

The tubes are packed with a catalyst containing 86% of TiO_2 , 4% of V_2O_5 and 10% of P_2O_5 and present in the form of pellets of 5 mm in diameter and from 5 to 20 mm in length.

The point of maximum temperature in the catalyst zone is 80 cm below the point of introduction of the gas. It is $530^\circ C$. The effluent gas is cooled in a gas cooler to $170^\circ C$ and then passes to a washing tower, into which a cooled aqueous maleic acid solution is sprayed through nozzles provided at a number of suitable positions. The gases are thus cooled to $38^\circ C$ and the maleic anhydride is washed out. The maleic acid solution is continuously withdrawn at a concentration of 35% and fresh water or dilute maleic acid solution obtained from the anhydridization stage is added at the same rate.

The 35% maleic acid is concentrated in a film evaporator at a pressure of 540 mm and a temperature of $135^\circ C$, to a concentration of 95%, the residence time being less than 3 minutes. The concentrate is then immediately passed to a second film evaporator in which the residual water is evaporated off at a pressure of 130 mm and a temperature of $160^\circ C$, the residence time being less than 5 minutes, accompanied by an-

hydridization of the maleic acid. Cooling the vapors to $110^\circ C$ produces crude maleic anhydride which is passed on for distillation. Further cooling to $70^\circ C$ produces an anhydride containing about 2% of water, and this is passed to the second film evaporator. The maleic anhydride which remains uncondensed due to its partial pressure is washed out with water, and the resulting approximately 2% maleic acid solution is passed to the washing tower in which the reaction gases were washed. The non-volatile or difficultly volatile constituents, about 4% of the maleic anhydride obtained, are withdrawn at the bottom of the film evaporator.

The crude maleic anhydride is fed to a column having 20 trays. The pressure is 70 mm. The anhydride is fed to the column at its 15th tray and pure maleic anhydride is withdrawn as a vapor above the 5th tray. The first runnings, comprising about 0.5% of the crude anhydride, are withdrawn at the top of the column.

The base of the column is maintained at $145^\circ C$ by a circulation evaporator and the higher boiling constituents, from about 1 to 2% of the material introduced, are continuously withdrawn. The yield of pure maleic anhydride is 350 kg/hr, that is, 45.5% of theory.

EXAMPLE 2

20,000 m^3/hr of air (STP), which has a temperature of about $100^\circ C$ due to the heat of compression, are passed, after the injection of 660 kg/hr of crude C_4 mixture containing approximately 3% of butadiene, 68% of n-butenes, 2% of isobutene and 27% of butanes, to the top of a tubular reactor together with 500 g/hr of triisobutyl phosphate. The reactor contains 5,500 tubes having a diameter of 25 mm and a length of 3 m. The tubes are surrounded by a bath comprising molten saltpetre. At the bottom and top of the reactor there are provided annular channels for the introduction and removal respectively of the molten salt. The melt flows countercurrently to the gas stream, leaving the reactor at its top and being recycled to the bottom thereof after cooling.

The temperature of the melt is maintained at $420^\circ C$.

The tubes are packed with a catalyst containing 86% of TiO_2 , 4% of V_2O_5 and 10% of P_2O_5 and present in the form of pellets of 5 mm in diameter and from 5 to 20 mm in length.

The point of maximum temperature in the catalyst zone is 80 cm below the point of introduction of the gas. It is $530^\circ C$. The effluent gas is cooled in a gas cooler to $180^\circ C$ and then passes to a washing tower, into which a cooled aqueous maleic acid solution is sprayed through nozzles provided at a number of suitable positions. The gases are thus cooled to $38^\circ C$ and the maleic

anhydride is washed out. The maleic acid solution is continuously withdrawn at a concentration of 35% and fresh water or dilute maleic acid solution obtained from the anhydridization stage is added at the same rate.

5 The 35% maleic acid is concentrated in a film evaporator at a pressure of 540 mm and a temperature of 135°C, to a concentration of 95%, the residence time being less than 3 minutes. The concentrate is then immediately passed to a second film evaporator in which the residual water is evaporated off at a pressure of 130 mm of Hg and a temperature of 160°C, the residence time being less than 5 minutes, accompanied by anhydridization of the maleic acid. Cooling the vapors to 110°C produces crude maleic anhydride which is passed on for distillation. Further cooling to 70°C produces an anhydride containing about 2% of water, and this is passed to the second film evaporator. The maleic anhydride which remains undissolved due to its partial pressure is washed out with water, and the resulting approximately 2% maleic acid solution is passed to the washing tower in which the reaction gases were washed. The non-volatile or difficultly volatile constituents, about 4% of the maleic anhydride obtained, are withdrawn at the bottom of the evaporator.

20 The crude maleic anhydride is fed to a column having 20 trays. The pressure is 70 mm. The anhydride is fed to the column at its 15th tray and pure maleic anhydride is withdrawn as a vapor above the 15th tray. The first runnings, comprising about 0.5% of the crude anhydride, are withdrawn at the top of the column.

35 The base of the column is maintained at 145°C by a circulation evaporator and the higher boiling constituents, from about 1 to 2% of the material introduced, are continuously withdrawn. Pure maleic anhydride is obtained in a yield of 45.5% of theory.

45 WHAT WE CLAIM IS:—

1. In a process for the continuous manufacture of maleic anhydride by oxidizing unsaturated straight-chained C_4 hydrocarbons with air in a tubular reactor in the presence of a catalyst containing titanium dioxide, vanadium pentoxide and phosphorus pentoxide, in which process the maleic anhydride formed is washed out of the reaction gases, the thus formed maleic acid is concentrated and then converted to the anhydride and the maleic anhydride is purified by continuous distillation, the improvement which comprises:

60 (a) using a mixture of C_4 hydrocarbons which contains at least 50% by weight of unbranched olefinically unsaturated C_4 hydrocarbons, adding this mixture to air heated to from 100° to 200°C,

whereupon a volatile inorganic or organic phosphorus compound is added. 65

(b) feeding this gas mixture to a tubular reactor in which the tubes are packed with a catalyst containing from 45 to 95% by weight of TiO_2 , from 0.2 to 20% by weight of V_2O_5 , and from 3 to 53% by weight of P_2O_5 , 70

(c) maintaining a temperature of from 420° to 600°C within the tubes, heat exchange being effected by a salt bath maintained at from 360° to 440°C, which salt bath is circulated through the reactor, evenly on all sides thereof, being fed to the reactor at one end through an annular channel and removed therefrom at the other end through a second annular channel. 75

(d) cooling the effluent reaction gases to 160° to 180°C and feeding the same to a washing tower in which the maleic anhydride is washed out by a circulated, cooled, aqueous maleic acid solution, concentrating the resultant 30 to 50% by weight maleic acid solution in one or more film evaporators arranged in cascade fashion to a concentration of more than 90% by weight and dissociating the concentrate in a further film evaporator to form maleic anhydride and steam, the removal of the water of reaction being carried out without inert entraining agents by direct entrainment by maleic anhydride vapors, and continuously distilling the cooled maleic anhydride obtained by fractional condensation in a distilling system. 80 85 90 95 100

2. A process as claimed in claim 1 wherein a mixture of C_4 hydrocarbons is used which contains at least 30% by weight of butadiene.

3. A process as claimed in claim 1 wherein a mixture of C_4 hydrocarbons is used which contains from 0 to 30% of butadiene, from 20 to 100% of n-butenes, from 0 to 40% of isobutene and from 10 to 50% of butanes, by weight, the sum of butadiene and n-butenes being at least 50% by weight. 105 110

4. A process as claimed in any of claims 1 to 3 wherein the catalyst consists of from 70 to 92% of TiO_2 , from 3 to 10% of V_2O_5 , and from 5 to 20% of P_2O_5 , by weight. 115

5. A process as claimed in any of claims 1 to 4 wherein the volatile organic phosphorus compound used is a trialkyl phosphate in which the alkyl radicals contain from 1 to 4 carbon atoms. 120

6. A process as claimed in any of claims 1 to 5 wherein there are added to the air heated at from 100° to 200°C from 25 to 40 g/m³ (STP) of the mixture of C_4 hydrocarbons. 125

7. A process for the continuous manufacture of maleic anhydride as claimed in claim 1 and substantially as hereinbefore described or exemplified.

5 8. Maleic anhydride when produced by a process as claimed in any of claims 1 to 7.

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